Single-molecule magnets: out-of-phase ac susceptibility signals from tetranuclear vanadium(III) complexes with an $S = 3$ ground state

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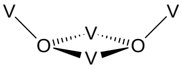
The salts of the tetranuclear vanadium(III) ions $[V_4O_2(O_2CEt)_7(L–L)_2]^z$ (L–L = bpy, $z = +1$; L–L = pic$^-$, $z = -1$) with a V_4 butterfly topology and a $S = 3$ ground state have been found to exhibit out-of-phase ac susceptibility signals, a signature of single-molecule magnets.

The study of molecules possessing unusually large spin values in their ground state is an area of intense current research, particularly since the realisation in recent years that some species with this property exhibit the new phenomenon of single-molecule magnetism.[1–4] Such molecules provide a new approach to nanoscale magnets, and one with the major advantage that it provides 'magnetic particles' that are both soluble and are composed of a single, sharply defined size. As such, they hold the promise of numerous technological applications, including access to the ultimate high-density memory device.

The first single-molecule magnet (SMM) to be discovered was $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]\cdot 2MeCO_2H\cdot 4H_2O$ with $S = 10$.[1–6] The related complexes $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_x]$ (R = Et, $x = 3$;[2] R = Ph, $x = 4$[2]) with $S = 9$ or 10 also show SMM properties, as does $[PPh_4][Mn_{12}O_{12}(O_2CEt)_{16}(H_2O)_4]$, the first ionic SMM.[2] More recently, a second class of SMM has been discovered, the family of Mn molecules of formulation $[Mn_4O_3X(O_2CMe)_3(dbm)_3]$ (X = various; dbm = anion of dibenzoylmethane) with a $[Mn_4(\mu_3\text{-}O)_3(\mu_3\text{-}X)]^{6+}$ highly distorted cubane core and an $S = 9/2$ ground state.[7] Additionally, $[Fe_8O_2(OH)_{12}(tacn)_6]^{8+}$ (tacn = 1,4,7-triazacyclononane) has been reported to exhibit SMM behaviour.[8] We recently reported the synthesis of $[V_4O_2(O_2CEt)_7(bpy)_2][ClO_4]$ **1** (bpy = 2,2′-bipyridine)[9] with a $[V_4O_2]^{8+}$ butterfly core and a $S = 3$ ground state, and we have now discovered that **1** and the related complex $[NEt_4][V_4O_2(O_2CEt)_7(pic)_2]$ **2** (pic = 2-picolinate) are new additions to this small family of SMMs.



Ac magnetic susceptibility studies, which monitor the response of a material's magnetic moment to an applied oscillating magnetic field, are an excellent way to detect the slow relaxation of magnetisation characteristic of a SMM. Ac susceptibility data were collected on **1** and **2** in a 1.0 G ac field oscillating at 250, 500 or 1000 Hz with a dc field of zero. In the range 10–30 K, the value of $\chi_m'T$ (χ_m' is the in-phase ac susceptibility) for **1** is constant at ~4.8 cm^3 K mol^{-1} ($\mu_{eff} = 6.20\ \mu_\beta$) consistent with an $S = 3$ ground state and $g \approx 1.8$. Below 4.0 K, $\chi_m'T$ decreases from 4.13 cm^3 K mol^{-1} at 4.0 K to 3.47 cm^3 K mol^{-1} at 1.7 K [Fig. 1(top)] suggesting that at these temperatures the magnetisation of the complex cannot reverse its direction fast enough to keep in phase with the oscillating ac field. If this is the case, an out-of-phase magnetic susceptibility (χ_m'') signal should be seen; indeed, a χ_m'' signal is observed [Fig. 1(bottom)] and found to be frequency dependent. Such behaviour is characteristic of single-molecule magnets, corresponding to superparamagnet-like behaviour normally associated with large, but single-domain collections of interacting spin carriers. However, the χ_m'' signal for **1** is quite weak at the lowest temperature attainable with present instrumentation, the χ_m'' value at 1.7 K being only *ca.* 1–2% of the χ_m' signal. Complex **2** gives similar results but a stronger χ_m'' signal of *ca.* 0.05 cm^3 K mol^{-1} at 1.7 K and a 1000 Hz ac field oscillation frequency.

As was the case for the $[Mn_{12}O_{12}]$ and $[Mn_4O_3X]$ complexes, the slow relaxation of **1** and **2** can be rationalized as due to a barrier to magnetisation reversal arising from a sufficiently large S coupled with negative magnetic anisotropy ($D < 0$, where D is the zero-field splitting (ZFS) parameter). For **1** and **2**, the potential energy plot of Fig. 2 then applies and indicates that the barrier to magnetisation reversal from, say, 'up' ($M_s = -3$) to down ($M_s = +3$) is $|9D|$. Fitting of dc magnetisation *vs.* field data (not shown) collected in the 0.500–50.0 kG and 2.00–30.0 K ranges gave $S = 3$, $g = 1.93$ and $D = -1.52$ cm^{-1} for **1**, and $S = 3$, $g = 2.00$ and $D = -1.50$ cm^{-1} for **2**. Thus, the barrier to magnetisation reversal in the ac experiments is $|9D| \approx 13.5$ cm^{-1}, a relatively small number that rationalises only a weak χ_m'' signal at 1.7 K. In contrast, the $S = 10$ and $D \approx -0.5$ cm^{-1} values for certain $[Mn_{12}O_{12}]$ complexes give a barrier of $|100D| \approx 50$ cm^{-1} and χ_m'' signals in the range 6–8 K under comparable conditions.[1–6]

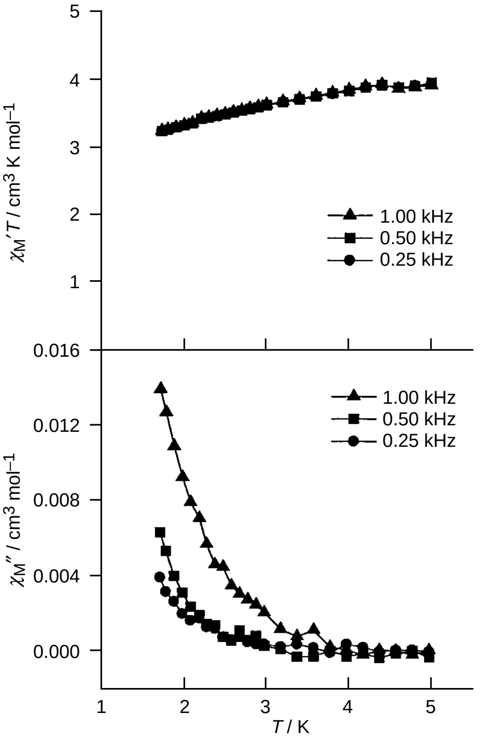


Fig. 1 Plots of $\chi_m'T$ *vs.* T (top) and χ_m'' *vs.* T (bottom) for $[V_4O_2(O_2CEt)_7(bpy)_2][ClO_4]$ **1** in a 1.0 G ac field oscillating at the indicated frequencies (and with no applied dc field)

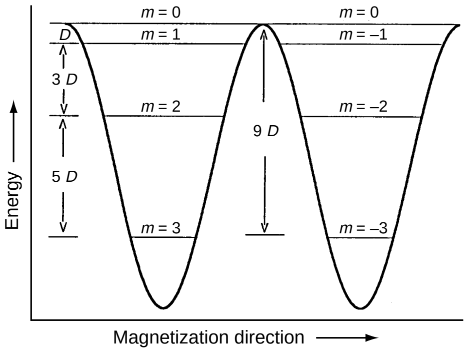


Fig. 2 Double-well potential energy *vs.* magnetisation direction diagram for an $S = 3$ system with a negative ZFS parameter D

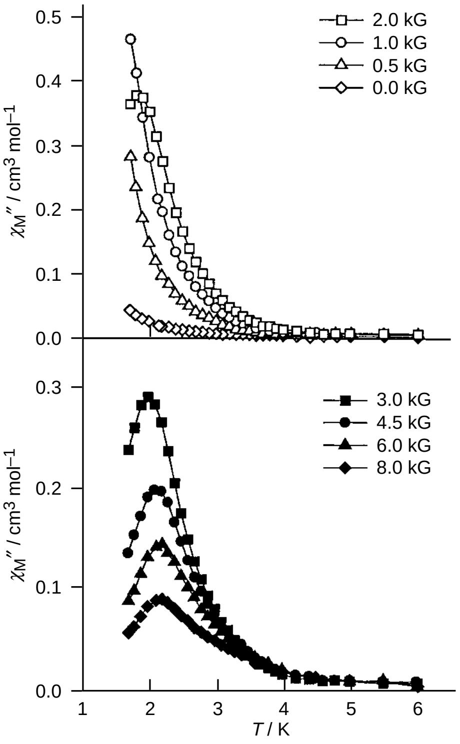


Fig. 3 Plots of χ_m'' *vs.* T for $[NEt_4][V_4O_2(O_2CEt)_7(pic)_2]$ **2** in a 1.0 G ac field oscillating at 1000 Hz and applied dc fields of 0–2.0 kG (top) and 3.0–8.0 kG (bottom)

To better observe the χ_m'' signals at $\geqslant$1.7 K, an external dc field was applied: this makes the double-well potential energy diagram of Fig. 2 asymmetric and slows down the relaxation rate by (*i*) increasing the barrier to (thermally activated) relaxation (originally $|9D|$), and (*ii*) making the energy levels on one side of the double-well no longer equienergetic to those on the other side, thus decreasing the rate of resonant quantum tunneling of magnetisation through the barrier. As a result, the χ_m'' signal should move to higher temperatures. This is indeed observed for **1** and **2**. The data for **2** at different dc fields are shown in Fig. 3 and it can be seen that the χ_m'' signal at 1.7 K increases in strength with increasing dc field, presumably as a χ_m'' peak moves closer to the observable temperature range. Eventually, a peak does become visible at 1.8 K at 2.0 kG dc field, moving to 2.2 K at 8.0 kG field. The peak position represents the temperature at which the relaxation rate equals the ac field frequency.

To probe the stability of complex **1** in solution, ^{1}H NMR spectra were recorded in CD_2Cl_2. A total of 20 peaks were observed in the range δ +90 to -50 assignable to the $[V_4O_2(O_2CEt)_7(bpy)_2]^+$ cation. This is exactly the number expected for effective C_2 solution symmetry: eight bpy resonances, four CH_3 resonances in a 2 : 2 : 2 : 1 relative integration ratio, and eight CH_2 resonances in a 2 : 2 : 2 : 2 : 2 : 2 : 1 : 1 relative ratio resulting from the diastereotopic nature of the CH_2 hydrogen atoms. The resonances were fully assigned by 2D COSY and T_1 studies, together with Me-substitution on the bpy rings: full details will be provided elsewhere.[10] Similar results were obtained for **2**. The ^{1}H NMR studies thus show that these cations retain their structures on dissolution.

The combined data described above establish that the $[V_4O_2]^{8+}$ complexes are new examples of single-molecule magnets and that they retain their structural and therefore magnetic integrity in solution. The latter is noteworthy, given that, in addition to a small, sharply defined size, solubility is one of the greatest advantages of SMMs over conventional magnetic particles of nanoscale dimensions.

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Notes and References

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